



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁴ : C10M 169/04, 141/12, 163/00 // (C10M 169/04, 105:06, 107:02 C10M 107:10, 135:02, 137:04 C10M 137:10, 139:00, 159:20 C10M 159:24) (C10M 141/12 C10M 129:10, 129:26, 135:02 C10M 137:04, 137:10, 139:00) (C10M 163/00, 135:02, 137:04 C10M 137:10, 139:00, 159:20 C10M 159:24)</p>	A2	<p>(11) International Publication Number: WO 87/ 05927</p> <p>(43) International Publication Date: 8 October 1987 (08.10.87)</p>
<p>(21) International Application Number: PCT/US87/00715</p> <p>(22) International Filing Date: 2 April 1987 (02.04.87)</p> <p>(31) Priority Application Number: 848,433</p> <p>(32) Priority Date: 4 April 1986 (04.04.86)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: THE LUBRIZOL CORPORATION [US/ US]; 29400 Lakeland Blvd., Wickliffe, OH 44092 (US).</p>	<p>(72) Inventors: SCHWIND, James, Jay ; 266 E. 323rd Street, Willowick, OH 44094 (US). TIPTON, Craig, Daniel ; 3595 Call Road, Perry, OH 44081 (US).</p> <p>(74) Agents: COLLINS, Forrest, L. et al.; The Lubrizol Cor- poration, 29400 Lakeland Blvd., Wickliffe, OH 44092 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (Eu- ropean patent), CH (European patent), DE (Euro- pean patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent).</p> <p>Published <i>Without international search report and to be repu- blished upon receipt of that report.</i></p>	
<p>(54) Title: LUBRICANT COMPOSITION</p> <p>(57) Abstract</p> <p>Manual transmission fluids having excellent static and dynamic frictional characteristics comprising: (a) an alkaline earth metal salt selected from the group consisting of sulfinates, phenates, oxylates, carboxylates and mixtures thereof; (b) a friction modifier selected from the group consisting of fatty phosphates, borated fatty epoxides, borated glycerol mono-carboxylates, borated alkoxylates fatty amines and mixtures thereof; (c) sulfurized olefin; and (d) a synthetic lubricant.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

-1-

LUBRICANT COMPOSITION

BACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates to a lubricating composition, and, in particular, to manual transmission fluids.

5 2. Description of the Art Practices

Transmission fluids, particularly those for synchro-mesh manual transmissions, have typically been based upon high weight mineral oils, e.g., 80 weight oil, engine oils, differential oils and automatic transmission fluids. The lighter of these oils, e.g., automatic transmission fluid, thins out too much at the high temperatures reached during summertime driving resulting in objectional gear noise. While the heavier of these oils are acceptable under normal summertime driving conditions, difficulties are often encountered in cold weather conditions. The viscosity of the heavier mineral oils increases substantially in the winter due to low temperatures. The shifting characteristics for the manual transmission are then significantly hindered due to the thickened oil. The hindered operation of the manual transmission requires greater effort to shift the gears. In extreme cases, this has resulted in a broken shifting lever.

A second problem which faces a synchromesh transmission is that of double detent or double bump. This phenomena results when the static coefficient of friction is too high and the cone and ring cannot engage due to insufficient slippage to allow smooth engaging. A further problem arises if the dynamic coefficient of friction is too low as clashing is observed. The clashing arises because the relative velocity of the blocker ring and cone assembly does not go to zero before engagement.

Given a resurgence of manual transmissions in an attempt to conserve fuel and in high performance vehicles using manual transmissions, it becomes imperative that the problems of double detent, low dynamic coefficient of

friction and high static coefficient of friction be solved. The present invention provides a solution to double detent through the formulation of a manual transmission fluid which exhibits high dynamic friction
5 properties as well as low static friction properties.

Various components of the present invention are known in lubricating fluids. For instance, United States Patent 4,031,023 issued June 21, 1977 to Musser and Koch, discloses the use of viscosity improvers to impart a
10 liquid character to a lubricating composition. Musser et al also discloses synthetic lubricating oils, extreme pressure (EP) agents and dispersants. The term dispersants as utilized by Musser et al include materials which suspend or disperse sludge and which are described
15 as being oil-soluble, and stably dispersible in lubricating compositions.

Heilman et al in United States Patent 3,957,664 issued May 18, 1976, discuss the use of olefin based synthetic lubricants. In particular, internal olefins or
20 mixtures of internal olefins are combined with di-t-butyl-p-cresol to obtain a high temperature lubricant.

Wiley et al in United States Patent 3,944,495 issued March 16, 1976, discuss various di-alkyl dithiophosphates obtained from oxylated long, straight-chain alcohols,
25 acids or mercaptans and the use of such materials in lubricating oils. Wiley et al is concerned with automatic transmission fluids and, in particular, zinc salts which are stated to give anti-corrossion and anti-wear properties to the automatic transmission.

30 United States Patent 4,119,550 issued October 10, 1978 to Davis and Holden describes sulfurized olefins as lubricant additives. A further disclosure of sulfurized olefins for use in lubricants is found in United States Patent 4,119,549 issued October 10, 1978 to Davis.

35 Further disclosures of sulfurized olefins for lubricant formulations are found in United States Patent 4,344,854 to Davis et al issued August 17, 1982. Still

further disclosures of sulfurized products useful in lubricants are found in Davis, United States Patent 4,191,659 issued March 4, 1980.

5 The use of calcium alkyl benzene sulfonates and polyolefins in a lubricant is found in United States Patent 4,172,855 issued October 30, 1979 to Shubkin et al. Horodysky, in United States Patent 4,529,528 issued July 16, 1985 describes borated amine-phosphite reaction products which are useful in lubricants and fuels.
10 Horodysky also discloses various olefin polymers which are stated to be useful in synthetic oils.

Howie et al, in United States Patent 4,525,289 issued June 25, 1985, discloses various lubricating formulations utilizing overbased calcium sulfonate and overbased
15 magnesium sulfonate. Trimers of alpha-decene are shown in combination with the sulfonate salts and as well with dispersants, foam inhibitors and amides in Howie et al.

The foregoing references, while generally applicable to lubricating compositions, do not specifically discuss
20 the issue of obtaining good dynamic and static properties in a manual transmission fluid. The present invention deals with obtaining a manual transmission fluid having outstanding static and dynamic frictional properties.

Throughout the specification and claims, percentages
25 and ratios are by weight, temperatures are in degrees Celsius, and pressures are in KPascals over ambient unless otherwise indicated. To the extent that references cited in the specification are relevant to the present invention, they are herein incorporated by reference.

SUMMARY OF THE INVENTION

The present invention describes a synthetic lubricant mixture suitable for a manual transmission fluid comprising:

- 5 (a) an alkaline earth metal salt selected from the group consisting of sulfonates, phenates, oxylates, carboxylates and mixtures thereof;
- (b) a friction modifier selected from the group consisting of fatty phosphites, borated fatty epoxides,
10 borated glycerol monocarboxylates, borated alkoxylated fatty amines and mixtures thereof;
- (c) a sulfurized olefin; and
- (d) a synthetic lubricant.

DETAILED DESCRIPTION OF THE INVENTION

The first aspect of the present invention is the alkaline earth metal salt which has been found particularly useful to assist in the frictional properties in the manual transmission fluid compositions. The salt may be a phenate, oxylate, carboxylate or preferably a sulfonate. It has been determined that the preferred salt is a magnesium sulfonate. Calcium salts are adequate for usage alone in the present invention but when used are preferably in combination with the magnesium sulfonate salts. Barium salts may also be used herein.

The sulfonate salts are those having a substantially oleophilic character and which are formed from organic materials. Organic sulfonates are well known materials in the lubricant and detergent arts. The sulfonate compound should contain on average from about 10 to about 40 carbon atoms, preferably from about 12 to about 36 carbon atoms and preferably from about 14 to about 32 carbon atoms on average. Similarly, the phenates, oxylates and carboxylates have a substantially oleophilic character.

While the present invention allows for the carbon atoms to be either aromatic or in a paraffinic configuration, it is highly preferred that alkylated aromatics be employed. While naphthalene based materials may be employed, the aromatic of choice is the benzene moiety.

The most preferred composition is thus a mono-sulfonated alkylated benzene, and is preferably the mono-alkylated benzene. Typically, alkyl benzene fractions are obtained from still bottom sources and are mono- or di-alkylated.

It is believed, in the present invention, that the mono-alkylated aromatics are superior to the di-alkylated aromatics in overall properties. The use of mono-functional (e.g., mono-sulfonated) materials avoids

-6-

crosslinking of the molecules with less precipitation of the salt in the transmission.

It is desired that a mixture of mono-alkylated aromatics (benzene) be utilized to obtain the mono-alkylated salt (benzene sulfonate) in the present invention. The mixtures wherein a substantial portion of the composition contains polymers of propylene as the source of the alkyl groups assists in the solubility of the salt in the manual transmission fluid.

The amount of the salt utilized in the present invention is typically from about 0.5% to about 8%, preferably from about 0.75% to about 6%, and most preferably from about 1% to about 5% by weight of the total composition. For maximum effectiveness, the salt should be greater than 3% by weight of the composition.

It is also desired that the salt be "overbased". By overbasing, it is meant that a stoichiometric excess of the alkaline earth metal be present over that required to neutralize the anion of the salt. The excess metal from overbasing has the effect of neutralizing acids which may build up in the lubricant. A second advantage is that the overbased salt increases the dynamic coefficient of friction. Typically, the excess alkaline earth metal will be present over that which is required to neutralize the anion at about 10:1 to 30:1, preferably 11:1 to 18:1 on an equivalent basis.

The second required component of the manual transmission fluid of the present invention is a friction modifier such as a fatty phosphite. The phosphites are generally of the formula $(RO)_2PHO$. The preferred dialkylated phosphite as shown in the preceding formula is typically present with a mono-alkylated phosphite of the formula $(RO)(HO)PHO$. Both of these phosphites are concomitantly produced and thus mixture of the mono-phosphite and the di-phosphite is present.

The mixtures of the phosphites are typically such that the weight ratio of the mono-phosphite to the

-7-

di-phosphite is from about 2:1 to about 1:4 by weight. It is, of course, highly desirable that the di-phosphite be present in an excess over the mono-phosphite.

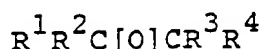
In the above structure of the phosphite, the term "R" has been referred to as an alkyl group. It is, of course, possible that the alkyl is alkenyl and thus the terms "alkyl" and "alkylated", as used herein, embrace other than saturated alkyl groups within the phosphite. The phosphite utilized herein is thus one having sufficient hydrocarbyl groups to render the phosphite substantially oleophilic and further that the hydrocarbyl groups are preferably substantially unbranched.

It is preferred that the phosphite contain from about 10 to about 24 carbon atoms in each of the fatty radicals described as "R". The inclusion of substantial amounts of the mono-alkylated phosphite require that the radical "R" contain a larger number of carbon atoms. Preferably, the fatty phosphite contains from about 12 to about 22 carbon atoms in each of the fatty radicals, most preferably from about 16 to about 20 carbon atoms in each of the fatty radicals. It is highly preferred that the fatty phosphite be formed from oleyl groups, thus having 18 carbon atoms in each fatty radical.

Other friction modifiers which are useful herein are borated fatty epoxides, borated glycerol monocarboxylates, and borated alkoxylated fatty amines. Borated fatty epoxides are known from Canadian Patent 1,188,704 issued June 11, 1985 to Davis. The oil-soluble boron-containing compositions of Davis are prepared by reacting at a temperature from about 80°C to about 250°C,

(A) at least one of boric acid or boron trioxide with

(B) at least one epoxide having the formula



-8-

wherein each of R^1 , R^2 , R^3 and R^4 is hydrogen or an aliphatic radical, or any two thereof together with the epoxy carbon atom or atoms to which they are attached, form a cyclic radical, said epoxide containing at least 8 carbon atoms.

As will be apparent, the borated fatty epoxides are characterized by the method for their preparation which involves the reaction of two materials. Reagent A may be boron trioxide or any of the various forms of boric acid, including metaboric acid (HBO_2), orthoboric acid (H_3BO_3) and tetraboric acid ($H_2B_4O_7$). Boric acid, and especially orthoboric acid, is preferred.

Reagent B is at least one epoxide having the above formula and containing at least 8 carbon atoms. In the formula, each of the R values is most often hydrogen or an aliphatic radical with at least one being an aliphatic radical containing at least 6 carbon atoms. The term "aliphatic radical" includes aliphatic hydrocarbon radicals (e.g., hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl, stearyl, hexenyl, oleyl), preferably free from acetylenic unsaturation; substituted aliphatic hydrocarbon radicals including substituents such as hydroxy, nitro, carbalkoxy, alkoxy and alkylthio (especially those containing a lower alkyl radical; i.e., one containing 7 carbon atoms or less); and hetero atom-containing radicals in which the hetero atoms may be, for example, oxygen, nitrogen or sulfur. The aliphatic radicals are preferably alkyl radicals, and more preferably those containing from about 10 to about 20 carbon atoms. Mixtures of epoxides may be used; for example, commercial available C_{14-16} or C_{14-18} epoxides and the like, wherein R^1 is a mixture of alkyl radicals having two less carbon atoms than the epoxide. Most desirably, R^1 is a straight-chain alkyl radical and especially the tetradecyl radical.

Further useful epoxides are those in which any two of the R radicals form a cyclic radical, which may be alicyclic or heterocyclic. Examples are n-butylcyclo-

pentene oxide, n-hexylcyclohexene oxide, methylenecyclo-octene oxide and 2-methylene-3-n-hexyltetrahydrofuran oxide.

5 The borated fatty epoxides may be prepared by merely blending the two reagents and heating them at a temperature from about 80° to about 250°C., preferably from about 100° to about 200°C., for a period of time sufficient for reaction to take place. If desired, the reaction may be effected in the presence of a substan-
10 tially inert, normally liquid organic diluent such as toluene, xylene, chlorobenzene, dimethylformamide or the like, but the use of such diluents is usually unnecessary. During the reaction, water is evolved and may be removed by distillation.

15 The molar ratio of reagent A to reagent B is generally between about 1:0.25 and about 1:4. Ratios between about 1:1 and about 1:3 are preferred, with 1:2 being an especially preferred ratio.

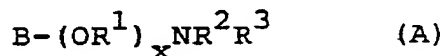
20 It is frequently advantageous to employ a catalytic amount of an alkaline reagent to facilitate the reaction. Suitable alkaline reagents include inorganic bases and basic salts such as sodium hydroxide, potassium hydroxide and sodium carbonate; metal alkoxides such as sodium methoxide, potassium t-butoxide and calcium ethoxide;
25 heterocyclic amines such as piperidine, morpholine and pyridine; and aliphatic amines such as n-butylamine, di-n-hexylamine and tri-n-butylamine. The preferred alkaline reagents are the aliphatic and heterocyclic amines and especially tertiary amines. When the preferred
30 method involving the "heel" is used, the alkaline reagent is typically added to the blend of the "heel" with reagent A.

35 The molecular structures of the compositions of this invention are not known with certainty. During their preparation, water is evolved in near-stoichiometric amounts for conversion of boric acid to boron trioxide when reagent A is boric acid, and gel permeation

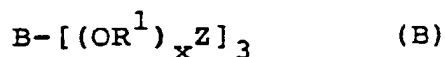
chromatography of the composition prepared from boric acid and a C₁₆ alpha-olefin oxide mixture in a 1:2 molar ratio indicates the presence in substantial amounts of three constituents having approximate molecular weights of 400, 600 and 1200.

The borated amines are generally known from European published applications 84 302 342.5 filed April 5, 1984 and 84 307 355.2 filed October 25, 1984, both authored by Reed Walsh.

The borated amine friction modifiers are conveniently prepared by the reaction of a boron compound selected from the group consisting of boric acid, boron trioxide and boric acid esters of the formula B(OR)₃ wherein R is a hydrocarbon-based radical containing from 1 to about 8 carbon atoms and preferably from about 1 to about 4 carbon atoms with an amine selected from the group consisting of hydroxy containing tertiary amines corresponding to the formulae



and



wherein Z is an imidazolen radical, R¹ in each formula is a lower alkylene based radical containing from 1 to about 8 carbon atoms, R² is a radical selected from the group consisting of hydrocarbon based radicals containing from 1 to about 100 carbon atoms and alkoxy radicals of the structure H(OR⁴)_y- where R⁴ is a lower alkylene based radical containing from 1 to about 8 carbon atoms, R³ and R⁵ (pendent from the ethylenic carbon in the 2 position in the imidazolen (Z) radical) are each hydrocarbon based radicals containing from 1 to about 100 carbon atoms, x and y are each an integer ranging from at least 1 to about 50 and the sum of x+y is at most 75. In a preferred embodiment, the amines useful in preparing the organo-borate additive compositions are those tertiary amines corresponding to (A) above wherein R² is an alkoxy

-11-

radical of the structure $H(OR^4)_y$ - wherein R^4 is a lower alkylene radical containing from 1 to about 8 carbon atoms and R^3 is an aliphatic based hydrocarbon radical containing from about 8 to about 25 carbon atoms, and preferably from about 10 to about 20 carbon atoms and x and y are each an integer ranging from at least 1 to about 25 and wherein the sum of x+y is at most 50, and those tertiary amines containing the imidazoline structure above wherein R^1 is a lower alkylene based radical containing from 1 to about 8 carbon atoms, R^5 is an aliphatic based hydrocarbon radical, preferably alkyl or alkenyl based radical, containing from about 8 to about 25 carbon atoms and preferably from about 10 to about 20 carbon atoms. Preferred tertiary amines useful in preparing the multi-functional organo-borate additive compositions are those tertiary amines corresponding to formula (A) above wherein R^2 is an alkoxy radical of the structure $H(OR^4)_y$ -, wherein R^1 and R^4 are individually ethylene or propylene radicals, R^3 is an alkyl or an alkenyl based hydrocarbon radical containing from about 10 to about 20 carbon atoms, x and y are each an integer ranging from at least 1 to about 9 and preferably from at least 1 to about 5 and the sum of x+y is at most 10 and preferably at most 5, i.e., the sum of x+y ranges from about 2 to about 10 and preferably from about 2 to about 5 respectively.

As used herein, the term "hydrocarbon-based radical" denotes a radical having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character within the context of this invention. Such radicals include the following:

(1) Hydrocarbon radicals; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic radicals, and the like, as well as cyclic radicals wherein the ring is completed through another portion of the molecule (that is, any two indicated hydrocarbon radicals,

-12-

e.g., R^2 and R^3 , may together form an alicyclic radical and such radical may contain heteroatoms such as nitrogen, oxygen and sulfur). Such radicals are known to those skilled in the art; representative examples are examples of such radicals as represented by R^2 , R^3 and R^5 in the formulae above include methyl, ethyl, butyl, hexyl, octyl, decyl, dodecyl, tetradecyl, octadecyl, eicosyl, cyclohexyl, phenyl and naphthyl and the like including all isomeric forms of such radicals and when R^2 and R^3 together form an alicyclic radical, then examples of such radicals include morpholinyl, piperidyl, piperazinyl, phenothiazinyl, pyrrolyl, pyrrolidyl, thiazolidinyl and the like.

(2) Substituted hydrocarbon radicals; that is, radicals containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the radical. Those skilled in the art will be aware of suitable substituents; representative examples are hydroxy (HO-); alkoxy (RO-); carbalkoxy (RO_2C -); acyl [$RC(O)$ -]; acyloxy (RCO_2 -); carboxamide ($H_2NC(O)$ -); acylimidazyl; [$RC(NR)$ -]; nitro- ($-NO_2$); and alkylthio (RS-) and halogen atoms (e.g., F, Cl, Br and I).

Hetero radicals; that is, radicals which, while predominantly hydrocarbon, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each 10 carbon atoms in the hydrocarbon-based radical.

Terms such as "alkyl-based radical," "alkenyl-based radical" and "alkylene-based radical" and the like have analogous meanings with respect to alkyl and aryl radicals and the like.

-13-

Representative examples of the tertiary amine compounds useful in preparing the organo-borate compounds of this invention include monoalkoxylated amines such as dimethylethanolamine, diethylethanolamine, dibutylethanolamine, diisopropylethanolamine, di(2-ethylhexyl)ethanolamine, phenylethylethanolamine, dibutylisopropanolamine, dimethylisopropanolamine and the like and polyalkoxylated amines such as methyldiethanolamine, ethyldiethanolamine, phenyldiethanolamine, diethyleneglycol mono-N-morpholinoethyl ether, N-(2-hydroxyethyl)thiazolidine, 3-morpholinopropyl-(2-hydroxyethyl)cocoamine, N-(2-hydroxyethyl)-N-tallow-3-aminomethylpropionate, N-(2-hydroxyethyl)-N-tallow acetamide, 2-oleoyl ethyl(2-hydroxyethyl) tallowamine, N-[N'-dodecenyl; N'-[2-hydroxyethylaminoethyl] thiazole, 2-methoxyethyl-(2-hydroxyethyl) tallowamine, 1-[N-dodecenyl; N-2-hydroxyethyl-aminoethyl] imidazole, N-[N'-octadecenyl-N'-2-hydroxyethyl-aminoethyl] phenothiazine, 2-hydroxydicocamine, 2-heptadecenyl-1-(2-hydroxyethylimidazoline, 2-dodecyl-1-(5-hydroxypentylimidazoline), 2-(3-cyclohexylpropyl)-1-(2-hydroxyethylimidazoline) and the like.

An especially preferred class of tertiary amines useful in preparing the organo-borate compounds of the invention is that constituting the commercial alkoxylated fatty amines known by the trademark "ETHOMEEN" and available from the Armak Company. Representative examples of these ETHOMEEN is ETHOMEEN C/12 (bis[2-hydroxyethyl] cocoamine); ETHOMEEN C/20 (polyoxyethylene[10]cocoamine); ETHOMEEN S/12 (bis[2-hydroxyethyl]soyamine); ETHOMEEN T/12 (bis[2-hydroxyethyl]tallowamine); ETHOMEEN T/15 (polyoxyethylene-[5]tallowamine); ETHOMEEN O/12 (bis[2-hydroxyethyl]oleyl-amine; ETHOMEEN 18/12 (bis[2-hydroxyethyl]octadecylamine; ETHOMEEN 18/25 (polyoxyethylene-[15]octadecylamine and the like. Of the various ETHOMEEN

-14-

compounds useful in preparing the organo-borate additive compounds of the invention, ETHOMEEN T/12 is most preferred.

5 If desired, the tertiary amine reactants represented by formulae (A) and (B) above may be reacted first with elemental sulfur to sulfurize any carbon-to-carbon double bond unsaturation which may be present in the hydrocarbon based radicals R^2 , R^3 and R^5 when these radicals are, for example, alkenyl radicals (e.g., fatty oil or fatty acid radicals).
10 Generally the sulfurization reaction will be carried out at temperatures ranging from about 100°C. to about 250°C. and preferably from about 150°C. to about 200°C. The molar ratio of sulfur to amine can range from about 0.5:1.0 to about 3.0:1.0 and preferably 1.0:1.0.
15 Although, generally no catalyst is required to promote sulfurization of any carbon-to-carbon double bond unsaturation which may be present in any tertiary amine reactant useful in preparing the organo-borate compositions of this invention, catalysts may be employed, if desired. If such catalysts are employed, preferably such catalysts are tertiary hydrocarbon substituted amines, most preferably, trialkylamines. Representative examples of which include tributylamine, dimethyloctylamine, triethylamine and the like.

25 The organo-borate additive friction modifiers can be prepared by adding the boron reactant, preferably boric acid, to at least one of the above defined tertiary amine reactants, in a suitable reaction vessel, and heating the resulting reaction mixture at a temperature ranging from
30 about 50° to about 300°C with continuous stirring. The reaction is continued until by-product water ceases to evolve from the reaction mixture indicating completion of the reaction. The removal of by-product water is facilitated by either blowing an inert gas, such as
35 nitrogen, over the surface of the reaction mixture or by conducting the reaction at reduced pressures. Preferably the reaction between the boron reactant and the tertiary

-15-

amine will be carried out at temperatures ranging from about 100°C to about 250°C and most preferably between about 150°C and 230°C while blowing with nitrogen.

Although normally the amines will be liquid at room temperature, in those instances where the amine reactant is a solid or semi-solid, it will be necessary to heat the amine to above its melting point in order to liquify it prior to the addition of the boron-containing reactant thereto. Those of ordinary skill in the art can readily determine the melting point of the amine either from the general literature or through a simple melting point analysis.

Generally, the amine reactant alone will serve as the solvent for the reaction mixture of the boron containing reactant and amine reactant. However, if desired, an inert normally liquid organic solvent can be used such as mineral oil, naphtha, benzene, toluene or xylene can be used as the reaction media. Where the organo-borate additive compound is to be added directly to a lubricating oil, it is generally preferred to conduct the reaction merely using the amine reactant as the sole solvent.

The borated fatty acid esters of glycerol are prepared by borating a fatty acid ester of glycerol with boric acid with removal of the water of reaction. Preferably, there is sufficient boron present such that each boron will react with from 1.5 to 2.5 hydroxyl groups present in the reaction mixture.

The reaction may be carried out at a temperature in the range of 60°C to 135°C, in the absence or presence of any suitable organic solvent such as methanol, benzene, xylenes, toluene, neutral oil and the like.

Fatty acid esters of glycerol can be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol tallowate, are manufactured on a commercial scale. The esters useful are oil-soluble and are preferably prepared from C₈ to C₂₂ fatty acid or mixtures thereof such as are

-16-

found in natural products. The fatty acid may be saturated or unsaturated. Certain compounds found in acids from natural sources may include licanic acid which contains one keto group. Most preferred C_8 to C_{22} fatty acids are those of the formula $RCOOH$ wherein R is alkyl or alkenyl.

The fatty acid monoester of glycerol is preferred, however, mixtures of mono- and diesters may be used. Preferably any mixture of mono- and diester contains at least 40% of the monoester. Most preferably, mixtures of mono- and diesters of glycerol contain from 40 to 60 percent by weight of the monoester. For example, commercial glycerol monooleate contains a mixture of from 45% to 55% by weight monoester and from 55% to 45% diester.

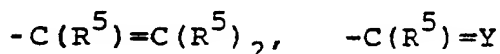
Preferred fatty acids are oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, linolenic, and eleostearic, and the acids from the natural products tallow, palm oil, olive oil, peanut oil, corn oil, neat's foot oil and the like. A particularly preferred acid is oleic acid. The borated fatty acid esters are conveniently stabilized against hydrolysis by reacting the esters with an alkyl or alkenyl mono- or bis-succinimide.

The amount of the friction modifier employed in the transmission fluids of the present invention is typically from about 0.1% to about 5%, preferably from about 0.25% to about 4%, and most preferably from about 0.5% to about 3.5% by weight of the total composition.

A sulfurized olefin is included in the present invention as an extreme pressure agent. Extreme pressure agents are materials which retain their character and prevent metal to metal damage, e.g., contact, when gears are engaged and meshed. The sulfurization of olefins is generally known as is evidenced by United States Patent 4,191,659 as previously disclosed.

-17-

The sulfurized olefins which are useful in the present invention are those materials formed from olefins which been reacted with sulfur. Thus, an olefin is defined as a compound having a double bond connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula $R^1R^2C=CR^3R^4$, wherein each of R^1 , R^2 , R^3 and R^4 is hydrogen or an organic radical. In general, the R values in the above formula which are not hydrogen may be satisfied by such groups as $-C(R^5)_3$, $-COOR^5$, $-CON(R^5)_2$, $-COON(R^5)_4$, $-COOM$, $-CN$, .



$-X$, $-YR^5$ or $-Ar$.

Each R^5 is independently hydrogen, alkyl, alkenyl, aryl, substituted alkyl, substituted alkenyl or substituted aryl, with the proviso that any two R^5 groups can be alkylene or substituted alkylene whereby a ring of up to about 12 carbon atoms is formed;

M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, magnesium, barium, calcium);

X is halogen (e.g., chloro, bromo, or iodo);

Y is oxygen or divalent sulfur; and

Ar is an aryl or substituted aryl radical of up to about 12 carbon atoms.

Any two of R^1 , R^2 , R^3 and R^4 may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

The nature of the substituents in the substituted moieties described above are not normally a critical aspect of the invention and any such substituent is useful so long as it is, or can be made compatible, with lubricating environments and does not interfere under the contemplated reaction conditions. Thus, substituted compounds which are so unstable as to deleteriously decompose under the reaction conditions employed are not

contemplated. However, certain substituents such as keto or aldehydo can desirably undergo sulfurization. The selection of suitable substituents is within the skill of the art or may be established through routine testing. Typical of such substituents include any of the above-listed moieties as well as hydroxy, amidine, amino, sulfonyl, sulfinyl, sulfonate, nitro, phosphate, phosphite, alkali metal mercapto and the like.

The olefinic compound is usually one in which each R value which is not hydrogen is independently alkyl, alkenyl or aryl, or (less often) a corresponding substituted radical. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R^3 and R^4 are hydrogen and R^1 and R^2 are alkyl or aryl, especially alkyl (that is, the olefin is aliphatic). Olefinic compounds having about 3 to 30 and especially about 3 to 18 (most often less than 9) carbon atoms are particularly desirable.

Isobutene, propylene and their oligomers such as dimers, trimers and tetramers, and mixtures thereof are especially preferred olefinic compounds. Of these compounds, isobutylene and diisobutylene are particularly desirable because of their availability and the particularly desirable because of their availability and the particularly high sulfur-containing compositions which can be prepared therefrom.

The sulfurization of such compounds is conducted as is known in the art and thus no further discussion of the sulfurized olefin component is given at this point.

The sulfurized olefins useful in the present invention as extreme pressure agents are typically utilized at from about 0.1% to about 5%, preferably from about 0.25% to about 4% and, most preferably from about 0.5% to about 3.5% by weight of the total composition.

-19-

Various sulfurized olefins which are useful in the present invention are shown in Table I below:

TABLE I

				% sulfur
5	Example	Olefinic compound	Molar ratio ¹	Temp., °C. in product
	(a)	Isobutene; 1-butene ²	1:1:0.5	171 46.9
	(b)	1-Octene	1:1.5:0.5	171 34.3
10	(c)	Isobutene; 1-octene ³	1:1:0.5	171 44.
	(d)	Diisobutene	1:1.5:0.5	171 41.
	(e)	C ₁₆ -C ₁₈ α-olefin	1:1.5:0.5	171 20.6
	(f)	Cyclohexene	1:1:0.5	171 31.8
15	(g)	Isobutene; 1-hexene ²	1:1:0.5	171 39.5
	(h)	Methyl oleate	1:1.5:0.5	171 16.5
	(i)	α-Methylstyrene	1:1:0.5	171 39.2
	(j)	Isobutene; butadiene ³	1:1:0.5	171 47.2
20	(k)	Polyisobutene ⁴	1:1.5:0.5	171 2.6
	(l)	Triisobutene ⁵	1:1.5:0.5	171 -
	(m)	1-Butene	1:1:0.5	138-171 49.5
	(n)	Isodecyl acrylate	1:0.5:0.5	171 13.1
25	(o)	Diels-Alder adduct of butadiene and butyle acrylate	1:1.5:0.5	171 25.1
	(p)	2-Butene ⁶	1:1:0.5	171 48.9
	(q)	Turpentine	1:1.5:0.5	171 39.2

30

¹ Olefinic compound(s):S:H₂S.

² 1:1 molar ratio.

³ 0.9:0.1 molar ratio.

⁴ Number average molecular weight of about 1000 as determined by vapor pressure osmometry.

35 ⁵ No separation step.

⁶ Cis and trans isomers.

The synthetic lubricating oils useful herein include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3 - C_8 fatty acid esters, or the C_{13} oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols

(e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-hexyl)-silicate, tetra-(p-tert-butylphenyl)silicate, hexyl-(4-methyl-2-pentoxo)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes, etc.). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans and the like.

Polyolefin oligomers are typically formed by the polymerization reaction of alpha-olefins. Nonalpha-olefins may be oligomerized to give a synthetic oil within the present invention, however, the reactivity and availability of alpha-olefins at low cost dictates their selection as the source of the oligomer.

The polyolefin oligomer synthetic lubricating oils of interest in the present invention include hydrocarbon oils and halo-substituted hydrocarbon oils such as are obtained

-22-

as the polymerized and interpolymerized olefins, e.g., oligomers, include the polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), similar materials and mixtures thereof.

Typically, the oligomer is obtained from a monomer containing from about 6 to 18 carbon atoms, preferably from about 8 carbon atoms to about 12 carbon atoms. Most preferably, the monomer used to form the oligomer is decene, and preferably 1-decene. The nomenclature alpha-olefin is a trivial name and the IUPAC nomenclature of a 1-ene compound may be considered to have the same meaning within the present invention.

While it is not essential that the oligomer be formed from an alpha-olefin, such is desirable. The reason for forming the oligomer from an alpha-olefin is that branching will naturally occur at the points where the olefin monomers are joined together and any additional branching within the backbone of the olefin can provide too high a viscosity of the end oil. It is also desirable that the polymer formed from the alpha olefin be hydrogenated. The hydrogenation is conducted according to known practices. By hydrogenating the polymer free radical attack on the allylic carbons remaining after polymerization is minimized.

The molecular weight of the oligomer is typically averages from about 250 to about 1400, conveniently from about 280 to about 1200 preferably from about 300 to about 1100 and most preferably about 340 to about 520. The choice of molecular weight of the oligomer is largely dependent upon whether a viscosity improver is included within the formulation. That is, the polyolefin oligomer, may require either a thickening or a thinning effect to ensure that the proper lubricating viscosities are maintained under extreme heat and cold conditions.

A further desirable synthetic lubricant is an alkylated aromatic compound. The alkylated aromatic

-23-

compounds are particularly beneficial in improving the low temperature flow characteristics. The alkylated aromatics may be referred to, supra, under the discussion of the alkaline earth metal salt. The alkylated aromatics are the same base materials utilized to manufacture the aromatic sulfonate.

The alkylated aromatic compound may be obtained in mixture with the sulfonate due to incomplete sulfonation of the alkylated aromatic. Of course, the alkylated aromatic may be obtained directly. Preferably, the aromatic nucleus of the alkylated aromatic compound is benzene. A particularly useful synthetic lubricant is a mixture of the alpha olefin oligomer and the alkylated aromatic. Typically, a mixture of the oligomer to the alkylated aromatic will be at a weight ratio of about 8:1 to about 1:8.

The amount of the synthetic lubricant which is employed in the present invention is typically from about 4% to about 98%, with intermediate ranges of about 7% to about 96%, and about 5% to about 95% by weight of the composition. The variability in the amount of the synthetic lubricant utilized in the present invention is largely because the synthetic lubricant may be obtained as a separate material with components A through C inclusive being utilized as a concentrate. That is, components A through C require more specialized processing conditions than the formation of the synthetic lubricant and thus it is often convenient to ship components A through C for blending with the synthetic lubricant. Where a concentrate is desired, components (A), (B) and (C) are conveniently obtained at from 95% to 50% by weight of the composition and the synthetic lubricant is obtained at 5% to 50% by weight of the composition.

Several additional components are desirably added to the manual transmission fluids of the present invention. Viscosity improving materials as previously referred to may be included in the compositions of the present

-24-

invention. The viscosity index improvers typically include polymerized and copolymerized alkyl methacrylates and mixed esters of styrene-maleic anhydride interpolymers reacted with nitrogen-containing compounds.

5 Polyisobutylene compounds are also typically used as viscosity index improvers. The amount of viscosity improver which may be typically added to the fully formulated manual transmission fluid composition is about 1% to about 50%, preferably about 10% to about 25% by weight.

10 Zinc salts are also added to manual transmission lubricants. Zinc salts are ordinarily utilized as extreme pressure agents such as zinc dithiophosphates. The zinc salts are added at levels measured by weight of the zinc metal at from about 0.02% to about 0.2%, preferably from about 0.04% to about 0.15% by weight.

Mineral oil such as 100 neutral oil may be included in the present invention. That is, it may be desirable as the mineral oil is less expensive than the oligomer to
20 formulate the composition removing a portion of the oligomer and replacing the same with the mineral oil. Thus, when mineral oil is utilized in the composition of the present invention, it may be present at from 0.1% to about 75%, preferably from about 0.5% to about 50% by weight of the total composition.

Additional ingredients which may be included in the manual transmission fluid of the present invention are fatty acid amides which are useful as additional friction modifiers, particularly for reducing the static
30 coefficient of friction. Further useful components herein include seal swell agents such as sulfones and sulfolanes. Suitable seal swell agents are disclosed in United States Patent 4,029,587 to Koch issued June 14, 1977. A still further useful component in the present invention is a
35 foam suppression agent such as a silicone oil. Any other typical ingredient may be included herein such as pour point depressants, dyes, odorants and the like.

-25-

The products of the present invention are obtained as a light orange, nearly clear liquid. Typical prior art manual transmission fluids will turn black after extended useage and a visible inspection is thus not possible. An
5 advantage to the compositions of the present invention is that the products may be visually examined for contaminants. Such contaminants may indicate the failure of seals or metal parts within the manual transmission. Thus a particular utility of the products of the present
10 invention in addition to being highly effective in having a high dynamic and a low static coefficient of friction is that they may be visually examined for deterioration of the transmission or contamination of the transmission fluid. The products herein are also of relatively low
15 viscosity at temperatures of -25°C and thus shift easily.

The products herein are primarily designed for manual transmission fluids although they may be used, where appropriate, for hydraulic fluids and other functional fluids.

20 The following are suggested examples of the present invention.

-26-

EXAMPLE I

A manual transmission fluid is prepared by combining the following ingredients:

- 5 56.5 parts of a poly alpha-olefin based on 1-decene monomer.
- 20 parts of a polyisobutylene having an average molecular weight (Mw) of approximately 1700.
- 15 parts of an alkylated benzene wherein the average alkyl chain is approximately 24 carbon atoms.
- 10 1 part of a maleic anhydride-styrene copolymer esterified as a pour point depressant.
- 100ppm foam inhibitor which is a polydimethyl siloxane.
- 1.0 part zinc dithiophosphate
- 15 0.75 part diolelyphosphite
- 1 part sulfurized olefin based on a mixture of 35 parts C₁₆₋₁₈ alpha-olefin, 63% soya oil and 2% oleic acid where the mixture has a sulfur content of 10% by weight
- 20 0.25 part fatty amide
- 0.3 part seal swell agent.
- 3.5 part magnesium alkyl benzene sulfonate (overbased) wherein the alkyl contains about 24 carbon atoms on average.
- 25 The product herein has a high dynamic coefficient of friction and a low static coefficient of friction. Cold weather viscosity is such that shifting is easily accomplished. The product is a light orange in color.

-27-

EXAMPLE II

A manual transmission fluid is prepared by combining the following ingredients:

- 5 56.5 parts of a poly alpha-olefin based on 1-decene monomer.
- 20 parts of a polyisobutylene having an average molecular weight (Mw) of approximately 1700.
- 15 parts of an alkylated benzene wherein the average alkyl chain is approximately 24 carbon atoms.
- 10 1 part of a maleic anhydride-styrene copolymer esterified as a pour point depressant.
- 100ppm foam inhibitor which is a polydimethyl siloxane.
- 1.0 part zinc dithiophosphate
- 15 0.5 part borated fatty (C₁₆) epoxide
- 1 part sulfurized olefin of Example I
- 0.25 part fatty amide
- 3.5 part magnesium alkyl benzene sulfonate (overbased) wherein the alkyl contains about 24 carbon atoms on average.
- 20

The product herein has a high dynamic coefficient of friction and a low static coefficient of friction. Cold weather viscosity is such that shifting is easily accomplished. The product is a light orange in color.

-28-

EXAMPLE III

A manual transmission fluid is prepared by combining the following ingredients:

- 5 56.5 parts of a poly alpha-olefin based on 1-decene monomer.
- 20 parts of a polyisobutylene having an average molecular weight (Mw) of approximately 1700.
- 15 parts of an alkylated benzene wherein the average alkyl chain is approximately 24 carbon atoms.
- 10 1 part of a maleic anhydride-styrene copolymer esterified as a pour point depressant.
- 100ppm foam inhibitor which is a polydimethyl siloxane.
- 1.0 part zinc dithiophosphate
- 15 0.5 part borated fatty (C₁₆) epoxide
- 1 part sulfurized olefin based on Example I
- 0.25 part fatty amide
- 3.5 parts calcium sulfur coupled alkyl (C₁₂) phenate overbased to 200 total base number.
- 20 The product herein has a high dynamic coefficient of friction and a low static coefficient of friction. Cold weather viscosity is such that shifting is easily accomplished. The product is a light orange in color.

EXAMPLE IV

A manual transmission fluid is prepared by combining the following ingredients:

- | | |
|----|---|
| 5 | 56.5 parts of a poly alpha-olefin based on 1-decene monomer. |
| | 20 parts of a polyisobutylene having an average molecular weight (Mw) of approximately 1700. |
| | 15 parts of an alkylated benzene wherein the average alkyl chain is approximately 24 carbon atoms. |
| 10 | 1 part of a maleic anhydride-styrene copolymer esterified as a pour point depressant. |
| | 100ppm foam inhibitor which is a polydimethyl siloxane. |
| | 1.0 part zinc dithiophosphate |
| 15 | 0.75 part dioleoylphosphite |
| | 1 part sulfurized olefin based on Example I |
| | 0.25 part fatty amide |
| 20 | 3.5 part calcium alkyl benzene sulfonate (overbased) wherein the alkyl contains about 24 carbon atoms on average. |

The product herein has a high dynamic coefficient of friction and a low static coefficient of friction. Cold weather viscosity is such that shifting is easily accomplished. The product is a light orange in color.

-30-

EXAMPLE V

A manual transmission fluid is prepared by combining the following ingredients:

- 5 56.5 parts of a poly alpha-olefin based on 1-decene monomer.
- 20 parts of a polymethacrylate having an average molecular weight (Mw) of approximately 1700.
- 15 parts of an alkylated benzene wherein the average alkyl chain is approximately 24 carbon atoms.
- 10 1. part of a maleic anhydride-styrene copolymer esterified as a pour point depressant.
- 100ppm foam inhibitor which is a polydimethyl siloxane.
- 1.0 part zinc dithiophosphate
- 15 0.75 part dioleoylphosphite
- 1 part sulfurized olefin based on a mixture of 35 parts C₁₆₋₁₈ alpha-olefin, 63% soya oil and 2% oleic acid where the mixture has a sulfur content of 10% by weight.
- 20 0.25 part fatty amide.
- 0.3 part seal swell agent.
- 3.5 part magnesium alkyl benzene sulfonate (overbased) wherein the alkyl contains about 24 carbon atoms on average.
- 25 The product herein has a high dynamic coefficient of friction and a low static coefficient of friction. Cold weather viscosity is such that shifting is easily accomplished. The product is a light orange in color.

What is claimed is:

1. A synthetic lubricant mixture suitable for a manual transmission fluid comprising:

5 (a) an alkaline earth metal salt selected from the group consisting of sulfonates, phenates, oxylates, carboxylates and mixtures thereof;

(b) a friction modifier selected from the group consisting of fatty phosphites, borated fatty epoxides, 10 borated glycerol monocarboxylates, borated alkoxyated fatty amines and mixtures thereof;

(c) a sulfurized olefin; and

(d) a synthetic lubricant.

2. The lubricant mixture of claim 1 containing a 15 fatty acid amide.

3. The lubricant mixture of claim 1 wherein the synthetic lubricant is selected from the group consisting of hydrocarbon oils, halosubstituted hydrocarbon oils, alkylene oxide polymers and interpolymers, alkylated 20 benzenes, esters of dicarboxylic and polycarboxylic acids, silicone-based oils, silicate based oils, esters of phosphorous containing acids, polymers of tetrahydrofuran and mixtures thereof.

4. The lubricant mixture of claim 1 wherein the 25 friction modifier is a fatty phosphite.

5. The lubricant mixture of claim 1 wherein alkaline earth metal salt is a magnesium salt.

6. The lubricant mixture of claim 3 wherein the hydrocarbon oil is a polyolefin oligomer.

-32-

7. The lubricant mixture of claim 4 wherein the fatty phosphite contains about 10 carbon atoms to about 24 carbon atoms in each of the fatty radicals.

5 8. The lubricant mixture of claim 5 wherein the salt is a magnesium sulfonate salt which contains an average alkyl chain length of about 10 to about 40 carbon atoms.

10 9. The lubricant mixture of claim 6 wherein the oligomer is obtained from a monomer having about 6 to about 18 carbon atoms.

10. The lubricant mixture of claim 1 wherein the alkaline earth metal salt is overbased.

15 11. The lubricant mixture of claim 7 wherein the fatty phosphite contains about 12 carbon atoms to about 22 carbon atoms in each of the fatty radicals.

12. The lubricant mixture of claim 9 wherein the oligomer is obtained from a monomer containing about 8 carbon atoms to about 12 carbon atoms.

20 13. The lubricant mixture of claim 8 wherein the magnesium sulfonate contains an aromatic nucleus.

14. The lubricant mixture of claim 1 wherein the alkaline earth metal salt is a magnesium salt.

15. The lubricant mixture of claim 1 wherein the alkaline earth metal salt is a calcium salt.

25 16. The lubricant mixture of claim 6 wherein the average molecular weight of the oligomer is about 340 to about 520.

17. The lubricant mixture of claim 1 containing a viscosity improver.

30 18. The lubricant mixture of claim 1 containing a zinc salt.

19. The lubricant mixture of claim 1 containing mineral oil.

35 20. The lubricant mixture of claim 1 wherein the synthetic lubricant is an alkylated aromatic.

21. The lubricant mixture of claim 18 wherein the zinc salt is zinc dithiophosphate.

-33-

22. The lubricant mixture of claim 13 wherein the aromatic nucleus is a benzene nucleus.

23. The lubricant mixture of claim 1 wherein:

5 (a) the alkaline earth metal salt is a magnesium sulfonate salt present at about 0.5% to about 8% by weight;

(b) the friction modifier is a fatty phosphite present at about 0.1% to about 5% by weight;

10 (c) the sulfurized olefin is present at about 0.1% to about 5% by weight; and

(d) the synthetic lubricant is a polyolefin oligomer present at about 4% to about 98% by weight.

24. The lubricant mixture of claim 1 containing a seal swell agent.

15 25. The lubricant mixture of claim 17 wherein the viscosity improver is a member selected from the group consisting of polyisobutylene and polymethacrylate and mixtures thereof.

20 26. The lubricant mixture of claim 20 wherein the alkylated aromatic is an alkyl benzene.

27. The lubricant mixture of claim 1 containing a foam suppressor.

28. The lubricant mixture of claim 24 wherein the seal swell agent is an oil soluble sulfone.

25 29. The lubricant mixture of claim 18 wherein the zinc salt is present at about 0.02% to about 0.2% by weight of the composition as zinc metal.

30 30. The lubricant mixture of claim 19 wherein the mineral oil is present at about 0.1% to about 75% by weight.

31. The lubricant mixture of claim 20 wherein the synthetic lubricant is a mixture of an alkylated aromatic and a polyolefin oligomer.

35 32. The lubricant mixture of claim 23 wherein the polyolefin oligomer is present at about 5% to about 95% by weight of the composition.

33. The lubricant mixture of claim 4 wherein the alkyl radicals in the fatty phosphite are substantially free of branching.

5 34. The lubricant mixture of claim 1 wherein the alkaline earth metal salt is a barium salt.

35. The lubricant mixture of claim 12 wherein the oligomer is obtained from a monomer which is 1-decene.

36. A concentrate containing about 95% to about 50% by weight of a mixture of (a), (b) and (c):

10 (a) an alkaline earth metal salt selected from the group consisting of sulfonates, phenates, oxylates, carboxylates and mixtures thereof;

(b) a friction modifier selected from the group consisting of fatty phosphites, borated fatty epoxides,
15 borated glycerol monocarboxylates, borated alkoxyated fatty amines and mixtures thereof;

(c) a sulfurized olefin; and

(d) from about 5% to about 50% by weight of a synthetic lubricant.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁴ : C10M 169/04, 141/12, 163/00 // (C10M 169/04, 105:06, 107:02 C10M 107:10, 135:02, 137:04 C10M 137:10, 139:00, 159:20 C10M 159:24) (C10M 141/12 C10M 129:10, 129:26, 135:02 C10M 137:04, 137:10, 139:00) (C10M 163/06 135:02, 137:04 C10M 137:10, 139:00, 159:20 C10M 159:24)</p>	A3	<p>(11) International Publication Number: WO 87/ 05927</p> <p>(43) International Publication Date: 8 October 1987 (08.10.87)</p>
<p>(21) International Application Number: PCT/US87/00715</p> <p>(22) International Filing Date: 2 April 1987 (02.04.87)</p> <p>(31) Priority Application Number: 848,433</p> <p>(32) Priority Date: 4 April 1986 (04.04.86)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: THE LUBRIZOL CORPORATION [US/ US]; 29400 Lakeland Blvd., Wickliffe, OH 44092 (US).</p>	<p>(72) Inventors: SCHWIND, James, Jay ; 266 E. 323rd Street, Willowick, OH 44094 (US). TIPTON, Craig, Daniel ; 3595 Call Road, Perry, OH 44081 (US).</p> <p>(74) Agents: COLLINS, Forrest, L. et al.; The Lubrizol Cor- poration, 29400 Lakeland Blvd., Wickliffe, OH 44092 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (Eu- ropean patent), CH (European patent), DE (Euro- pean patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent).</p> <p>Published <i>With international search report.</i></p> <p>(88) Date of publication of the international search report: 24 March 1988 (24.03.88)</p>	
<p>(54) Title: LUBRICANT COMPOSITION</p> <p>(57) Abstract</p> <p>Manual transmission fluids having excellent static and dynamic frictional characteristics comprising: (a) an alkaline earth metal salt selected from the group consisting of sulfinates, phenates, oxylates, carboxylates and mixtures thereof; (b) a friction modifier selected from the group consisting of fatty phosphates, borated fatty epoxides, borated glycerol mono-carboxylates, borated alkoxyates fatty amines and mixtures thereof; (c) sulfurized olefin; and (d) a synthetic lubricant.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

INTERNATIONAL SEARCH REPORT

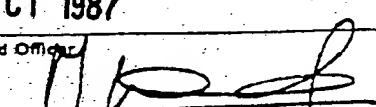
-2-

International Application No PCT/US 87/00715

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC⁴ (C 10 M 163/06, 135:02, 137:04, 137:10, 139:00, 159:20, 159:24)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System ¹	Classification Symbols	
IPC ⁴	C 10 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X, L	US, A, 4344854 (K.E. DAVIS et al.) 17 August 1982 see abstract; column 1, lines 21-50; column 5, lines 26-32; column 7, lines 26-62; column 8, lines 24-51; column 8, line 62 - column 9, line 19; column 9, line 56 - column 10, line 68; column 11, line 26 - column 12, line 27; examples A-F; claims 26, 33, 38	1-7, 9-12, 14, 15, 18- 21, 23, 25- 27, 29, 32- 36
Y	cited in the application	8, 13, 16, 19, 22, 30, 31
--		
X, L	US, A, 4031023 (J.L. MUSSER & F.W. KOCH) 21 June 1977 see abstract; column 1, line 23 - column 2, line 48; column 7, line 62 - column 11, line 59; column 15, line 51 - column 17, line 65; column 18, line 18 - column 19, line 29; column 19, line 52 - column 20, line 63; column 21, lines 3-25; examples A, C, E, G, H; claims 14, 19-21, 24	1-7, 9-12, 14, 15, 17- 21, 23-27, 32-36
Y	cited in the application	8, 13, 16, 22, 28-31
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
21st September 1987		
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/00715

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC C 10 M 169/04; C 10 M 141/12; C 10 M 163/00; //(C 10 M 169/04, IPC ⁴ : 105:06, 107:02, 107:10 135:02, 137:04, 137:10, 139:00, 159:20, 159:24; (C 10 M 141/12, 129:10, 129:26, 135:02, 137:04, 137:10, 139:00);		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁴	C 10 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ** with Indication, where appropriate, of the relevant passages. **	Relevant to Claim No. **
X, L	US, A, 4119550 (K.E. DAVIS et al.) 10 October 1978 see abstract; column 1, lines 19-51; column 7, lines 21-27, 34-38, 44-61; column 8, lines 4-39; column 8, line 62 - column 9, line 35; column 5, lines 55-65; column 10, line 43 - column 11, line 11; examples A-F	1-7, 9-12, 14, 15, 18, 20, 21, 23, 26-29, 32- 36
Y	cited in the application	8, 13, 16, 19, 22, 30, 31
X, L	US, A, 4191659 (K.E. DAVIS) 4 March 1980 see abstract; column 1, lines 46-55; column 2, lines 49-65; column 5, lines 27-36; column 7, lines 57-63; column 8, line 27 - column 9, line 31; column 9, line 54 - column 10, line 19; column 11, lines 28-45; column 11, line 62 - column 12, line 29; examples A-D; claims 32, 44	1, 3-7, 9-15, 17, 18, 20, 21, 23, 26, 27, 29, 32- 36
Y	cited in the application	8, 13, 16, 19, 22, 30, 31
<p>* Special categories of cited documents:--</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
21st September 1987	13 OCT 1987	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN MOL 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	FR, A, 2315537 (THE LUBRIZOL CORPORATION) 21 January 1977 see page 1, line 1 - page 2, line 13; page 2, lines 20-25; page 2, line 34 - page 4, line 21; page 7, line 15 - page 8, line 16; page 9, line 1 - page 10, line 7; claims 1,8 & US, A, 4029587 (cited in the application) --	28
Y	US, A, 4172855 (R.L. SHUBKIN et al.) 30 October 1979 see abstract; column 7, lines 15-28, 39-43 cited in the application --	8,13,16,19, 22,30,31
Y	US, A, 3957664 (W.J. HEILMANN et al.) 18 May 1976 see column 1, lines 7-15; column 2, lines 37-63; column 3, lines 12-17; column 12, line 61 - column 14, line 24; claim 5 A cited in the application --	16 23,32
Y	CA, A, 1188704 (LUBRIZOL CORPORATION) 11 June 1985 see page 1, lines 1-18; page 2, lines 16-33; page 8, lines 1-4,10-14; page 8, line 19 - page 15, line 6 cited in the application --	1-36
Y	EP, A, 0157969 (THE LUBRIZOL CORPORATION) 16 October 1985 see abstract; page 1, line 7 - page 4, line 23; page 9, lines 16-36; page 11, lines 1-30; page 12, line 1 - page 13, line 24; page 14, line 11 - page 15, line 19; page 16, lines 5-21; page 17, line 1 - page 18, line 7; examples 18,23 cited in the application --	1-36
A	GB, A, 2102023 (CHEVRON RESEARCH CO.) 26 January 1983 see abstract; page 5, lines 1-34; claims 1,6-12 --	1,19,20,30, 33,36
Y	EP, A, 0067002 (THE LUBRIZOL CORPORATION) 15 December 1982 see abstract; page 8, line 1 - page 10, line 22; page 11, line 10 - page 16, line 14; claims 17-20 -----	1-36

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 87/00715 (SA 16967)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 05/10/87.

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4119550	10/10/78	BE-A- 870255	06/03/79
		US-A- 4344854	17/08/82
		US-A- 4191659	04/03/80
		US-A- 4119549	10/10/78
US-A- 4191659	04/03/80	US-A- 4119549	10/10/78
		US-A- 4119550	10/10/78
US-A- 4344854	17/08/82	BE-A- 870254	06/03/79
		US-A- 4119549	10/10/78
		US-A- 4119550	10/10/78
		BE-A- 870255	06/03/79
US-A- 4031023	21/06/77	FR-A, B 2341644	16/09/77
		DE-A, C 2705877	01/09/77
		GB-A- 1521026	09/08/78
		AU-A- 2246077	24/08/78
		JP-A- 52100504	23/08/77
		CA-A- 1103653	23/06/81
		AU-B- 514458	12/02/81
FR-A- 2315537	21/01/77	DE-A- 2627226	20/01/77
		US-A- 4029587	14/06/77
		GB-A- 1532458	15/11/78
		CA-A- 1058151	10/07/79
		JP-A- 52003585	12/01/77
		US-A- 4029588	14/06/77
US-A- 4172855	30/10/79	None	
US-A- 3957664	18/05/76	US-A- 3876720	08/04/75
		US-A- 3907922	23/09/75
CA-A- 1188704	11/06/85	EP-A, B 0067002	15/12/82
		JP-A- 57200496	08/12/82
		US-A- 4584115	22/04/86
EP-A- 0157969	16/10/85	JP-A- 60229995	15/11/85
GB-A- 2102023	26/01/83	FR-A, B 2508926	07/01/83

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82

INTERNATIONAL APPLICATION NO.
-----PCT/US 87/00715 (SA 16967)

		BE-A-	893728	03/11/82
		SE-A-	8204019	29/06/82
		JP-A-	58008798	18/01/83
		AU-A-	8359582	06/01/83
		DE-A-	3224317	03/02/83
		NL-A-	8202641	01/02/83
		CA-A-	1177472	06/11/84
		US-A-	4495088	22/01/85
		AU-B-	549639	06/02/86

EP-A- 0067002	15/12/82	JP-A-	57200496	08/12/82
		CA-A-	1188704	11/06/85
		US-A-	4584115	22/04/86

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82

